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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in and relating to Surface Coating

We, COURTAULDS LIMITED, a British Company, of 18 Hanover Square, London, W.1, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with a surface coating process and thermally curable surface coating compositions of the kind known as stoving compositions.

The stoving compositions of this invention differ from known compositions in that they contain little or none of the volatile solvents which constitute the vehicle of the known compositions.

According to the present invention a surface coating composition comprises a curable binder dissolved in an unsaturated ester which conforms to the following general formula:

$$CH_2=C(R)-CH_2-O-R^1-OOC-R^2$$

in which R is hydrogen or alkyl, R^1 is alkylene and R^2 is an aliphatic radical containing at least one carbon-to-carbon double bond, the ester being liquid at room temperature, having a boiling point of at least 200°C. and a molecular weight of less than 800.

The present invention also includes a surface coating process comprising coating a surface with an unsaturated ester conforming to the general formula:

$$CH_2=C(R)-CH_2-O-R^1-OOC-R^2$$

in which R, R^1 and R^2 have the meanings given them above, and heating the coated surface to cure the ester.

In the above formula, for example, R may be methyl or ethyl, R^1 ethylene or propylene and R^2 may be alkenyl or substituted alkenyl, e.g. vinyl, propenyl, butenyl or pentenyl. The more important esters are derivatives of a dibasic acid in which the radical —OOC—R^2 of the above formula represents the radical —OOC—R^3—$COOR^4$ in which R^3 is a direct bond, or alkylene or alkenylene and R^4 is alkyl or alkenyl, it being understood that when R^3 is a cipher or alkylene, R^4 must be alkenyl. Specific examples of the esters are:

Allyloxyethyl acrylate
Allyloxyethyl methacrylate
Methallyloxyethyl methacrylate
Di-allyloxyethyl itaconate
Di-allyloxyethyl oxalate
Di-allyloxyethyl succinate
Di-methallyloxyethyl fumarate
Di-allyloxyethyl maleate
Di-allyloxypropyl fumarate
Di-allyloxyethyl adipate

It will be seen that the listed esters are examples of a group consisting of alcohols of the general formula:

$$CH_2=C(R)-CH_2-O-R^1-OH$$

esterified with unsaturated monocarboxylic acids or with dicarboxylic acids which may or may not contain ethylenic unsaturation. The group, therefore, consists of esters which contain two or three carbon-to-carbon double bonds. Suitable alcohols include allyloxyethanol, allyloxypropanol, methallyloxyethanol and methallyloxypropanol.

The surface coating may consist of one or more unsaturated esters, but, in general, the viscosity of such a coating is too low to be widely applicable. A preferred surface coating having a higher viscosity comprises a

[*Price 5s.*]

curable binder dissolved in the unsaturated ester or esters: for example the binder may be an alkyd resin or styrenated alkyd resin or linear unsaturated polyester. The surface coating may in addition contain a pigment and air-drying catalysts for example soluble compounds of cobalt and manganese.

During the stoving operation the unsaturated esters are able to interact in the presence of oxygen to produce a crosslinked polymer; that is the liquid film of the surface coating composition formed on the object to be painted may be cured to a solvent-resistant condition by stoving. When a binder is incorporated in the coating, the stoving induces a polymerisation reaction between the binder and the ester or esters so that the coating is homogeneously cured.

Although the unsaturated esters function as solvents for the binders in the preferred coatings, this is the only function they have in common with the solvents or solvent vehicles of known coatings. The unsaturated esters have boiling points which do not allow the esters to evaporate to any significant extent at accepted stoving temperatures, say between 140° and 160°C. Furthermore, the unsaturated esters are chemically modified and embodied in the cured coating, whereas the vehicle in known coatings is evaporated and is not present in the cured coating either *per se* or in a chemically modified condition. In the application of the surface coating composition, therefore, it is unnecessary to take the stringent precautions which usually accompany the dipping and spraying of objects with a conventional solvent-based coating; there is little or no vapour of inflammable or poisonous materials to contaminate the atmosphere and no requirement for the recovery of evaporated solvent.

The hardness of the cured film may be altered within wide limits by the relative proportions of doubly unsaturated and triply unsaturated esters, but it has also proved possible to reduce the incidence of crosslinks to below the value obtained in a composition employing only doubly unsaturated esters, by introducing a mono-ethylenically unsaturated ester particularly an ester of an alcohol according to the previously noted general formula:

$$CH_2=C(R)-CH_2-O-R^1-OH$$

Alcohols of this kind, esterified with saturated mono-basic carboxylic acids, particularly when the acid contains from 6 to 18 carbon atoms, are found to increase the flexibility of the stoved film.

Suitable esters of this type may conform to the formula:

$$CH_2=C(R)-CH_2-O-R^1-OOCR^5$$

where R is hydrogen or alkyl, R^1 is alkylene and R^5 is alkyl or aryl.

The relative proportions of the esters which differ in the number of ethylenically unsaturated groups they contain, affects the properties of the stoved film: generally speaking, the esters containing multiple unsaturation increase the hardness of the film and those having only single ethylenic unsaturation increase the flexibility.

The invention is illustrated by the following Examples.

Example 1

Diallyloxypropyl fumarate was prepared by esterifying fumaric acid with allyloxypropanol. An 0.002 inch thick film of this ester was laid down on a mild steel panel, and baked in an oven at 150°C for 15 minutes. At the end of this time the ester had cured to a clear, water-white film which was not scratched when a 4H pencil was drawn across it.

Example 2

Diallyloxyethyl itaconate was prepared by esterifying itaconic acid with allyloxyethanol. The ester was laid down on a mild steel panel as a film of 0.003 inch thickness and baked in an oven at 150°C for 15 minutes. The cured ester was a clear, water-white film having a hardness greater than a 4H pencil as determined in Example 1.

Example 3

An unsaturated fatty acid modified alkyd was prepared from 140 parts by weight of safflower fatty acids, 65 parts of itaconic acid and 81 parts of trimethylolpropane by condensation at from 160° to 180°C and in the presence of a minor proportion of cyclohexane as water entrainer. Condensation and elimination of water were continued until the alkyd had an acid value of 16. At this stage cyclohexane was removed by distillation and the alkyd was dissolved in an equal weight of diallyloxypropyl fumarate.

An 0.005 inch thick film of the solution was laid down on a mild steel panel and baked in an oven at 160°C for 30 minutes. The clear cured film had a pale yellow colour and a hardness of 2H, that is the film was not scratched by a 2H pencil but was scratched by a 3H pencil.

WHAT WE CLAIM IS:—

1. A thermally-curable surface coating composition comprising a curable binder dissolved in an unsaturated ester conforming to the general formula:

$$CH_2=C(R)-CH_2-O-R^1-OOC-R^2$$

in which R is hydrogen or alkyl, R^1 is alkylene and R^2 is an aliphatic radical containing at least one carbon-to-carbon double bond, the ester being liquid at room temperature, having a boiling point of at least 200°C and a molecular weight of less than 800.

2. A surface coating composition as claimed in claim 1 in which the unsaturated ester conforms to the formula:

$$CH_2=C(R)-CH_2-O-R^1-OOC-R^3-COOR^4$$

in which R^3 is a direct bond, or alkylene or alkenylene and R^4 is alkyl or alkenyl, provided that at least one of R^3 and R^4 contains a carbon-to-carbon double bond.

3. A surface coating composition as claimed in either of the preceding claims in which the ester is that of a dicarboxylic acid esterified with allyloxyethanol, allyloxypropanol, methallyloxyethanol or methallyloxypropanol.

4. A surface coating composition as claimed in claim 3 in which the ester is that of a saturated dicarboxylic acid.

5. A surface coating composition as claimed in any of the preceding claims in which the binder is an alkyd resin, styrenated alkyd resin or linear unsaturated polyester.

6. A surface coating composition as claimed in any preceding claim which also comprises an ester having one carbon-to-carbon double bond.

7. A surface coating composition as claimed in claim 6 in which the ester conforms to the formula:

$$CH_2=C(R)-CH_2-O-R^1-OOCR^5$$

where R is hydrogen or alkyl, R^1 is alkylene and R^5 is alkyl or aryl.

8. A surface coating process comprising coating a surface with an unsaturated ester conforming to the general formula:

$$CH_2=C(R)-CH_2-O-R^1-OOC-R^2$$

in which R, R^1 and R^2 have the meanings given them in claim 1, and heating the coated surface to cure the ester.

9. A surface coating process as claimed in claim 8 comprising coating a surface with a surface coating composition as claimed in any of claims 1 to 7, and heating the coated surface to cure the coating.

10. A surface coating process as claimed in claim 8 carried out substantially as described in any of the Examples.

11. An article coated with a surface coating by a surface coating process as claimed in any of claims 8 to 10.

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